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KETO COMPLEXES FROM THE OXIDATION OF η^6-XANTHENE OR THIOXANTHENE-η^5-CYCLOPENTADIENYLIRON CATION AND SOME REACTIONS OF THE FLUORENONE AND XANTHONE COMPLEXES

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Summary

Ligand exchange between xanthene and ferrocene gave the η^6-xanthene-η^5-cyclopentadienyliron cation which was oxidized in situ with $KMnO_4$ to give the η^6-xanthone-η^5-cyclopentadienyliron cation (III). Similar oxidation of the η^6-thioxanthene-η^5-cyclopentadienyliron cation gave a mixture of the thioxanthone complex IV and the corresponding complexed sulfone V. III and the η^6-fluorenone-η^5-cyclopentadienyliron cation (VI) were utilized as reactants in the synthesis of new complexes via reactions with a number of reagents. Stereospecific *exo*-addition to give complexed *endo*-alcohols were observed in the reaction of III with $NaBH_4$, $NaBD_4$ or CH_3Li, and in the reaction of VI with CH_3Li, the anion of acetonitrile, the anion of nitromethane or the phenylacetylide anion. Ring opening reactions to give complexed *o,o'*-disubstituted benzophenones were observed when III was treated with the anion of acetonitrile, the anion of nitromethane, methylamine, cyclohexylamine, benzylamine or pyrrolidine.

Introduction

Recently, we have reported that η^6-ketoarene-η^5-cyclopentadienyliron cations could be prepared from the $KMnO_4$ oxidation of the aqueous solution of the tetrachloroaluminate salts of η^6-arene-η^5-cyclopentadienyliron cations derived from ligand exchange reactions without the prior isolation of the product from the ligand exchange [1]. Methylene groups α to the complexed aromatic ring were oxidized to carbonyl functions. Ketoarene complexes successfully prepared in this way include the cyclopentadienyliron (CpFe) complexes of fluorenone, anthraquinone and benzophenone. In the present work, we have extended such studies by investigating the $KMnO_4$ oxidation of complexes with an heterocyclic ligand, namely, the oxidation of the η^6-xanthene or thioxanthene-η^5-cyclopentadienyliron cation. Some reactions

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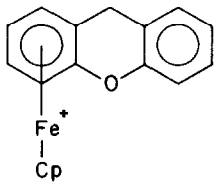
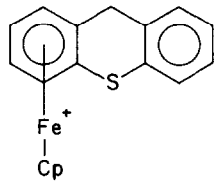
of two typical keto complexes, the CpFe complexes of fluorenone and xanthone, have also been studied.

Results and discussion

The ligand exchange reaction between ferrocene and xanthene or thioxanthene [2] gave the η^6-xanthene-η^5-cyclopentadienyliron cation (I) or the η^6-thioxanthene-η^5-cyclopentadienyliron cation (II). These cations were oxidized in situ without their

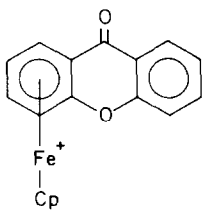


I

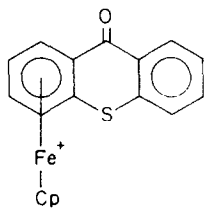


II

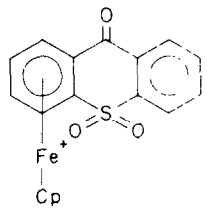
prior isolation by treatment with $KMnO_4$ [1]. The xanthone complex III was obtained from the oxidation of I while the oxidation of II gave a mixture of the thioxanthone complex IV and the corresponding sulfone complex V. When about 0.8 molar equivalent of $KMnO_4$ was used in the oxidation of II, a 7/3 ratio of IV/V was obtained, and when the amount of $KMnO_4$ was raised to 1.2 molar equivalents, the ratio of IV/V was about 1/4. By washing the mixture of the hexafluorophosphate salts of IV and V with acetone, IV could be removed, thus effecting a separation of IV and V.



III



IV



V

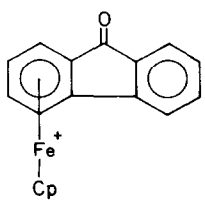
TABLE 1

^{1}H NMR CHEMICAL SHIFTS AND IR CARBONYL ABSORPTIONS OF THE HEXAFLUOROPHOSPHATE SALTS OF KETO COMPLEXES III, IV AND V

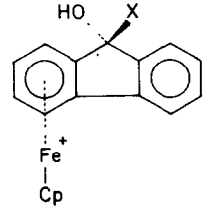
Complex	$\delta(CD_3CN)$ (ppm from TMS)			IR ν(CO) (cm^{-1})
	Cp	Complexed aromatic	Uncomplexed aromatic	
Xanthone-$FeCp^+$ (III)	5.0(s,5H)	6.3–6.7(m,2H) 6.8–7.1(m,2H)	7.4–7.7(m,2H) 7.8–8.1(m,1H) 8.2–8.4(m,1H)	1675
Thioxanthone-$FeCp^+$ (IV)	4.9(s,5H)	6.5–6.7(m,2H) 6.7–6.9(m,1H) 6.9–7.3(m,1H)	7.3–7.8(m,3H) 8.4–8.6(m,1H)	1675
Thioxanthen-9-one-10,10-dioxide-$FeCp^+$ (V)	5.3(s,5H)	6.8–7.1(m,2H) 7.2–7.4(m,2H)	7.7–8.6(m,4H)	1680

Given in Table 1 are the ^1H NMR chemical shifts and the carbonyl IR absorptions for the hexafluorophosphate salts of III, IV, and V, while Table 2 summarizes the ^{13}C NMR data. For comparison, the ^{13}C absorptions for the free keto ligands, xanthone [3], thioxanthone [3], and thioxanthen-9-one-10,10-dioxide, are also included in Table 2. These spectral data are consistent with the structures assigned to III, IV, and V. Moreover, these complexes, upon pyrolytic sublimation under reduced pressure [4], gave the liberated known free ligands, xanthone, thioxanthone, and thioxanthen-9-one-10,10-dioxide, further confirming the structures of III, IV, and V.

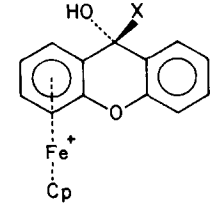
In our previous work [1], it was reported that the treatment of a ketoarene complex with $NaBH_4$ or $NaBD_4$ resulted in the stereospecific *exo*-attack by the hydride or deuteride ion on the carbonyl function to give the complexed *endo*-al-



VI



VII a X = H
b X = D
c X = CH_3



VIII a X = H
b X = D
c X = CH_3

TABLE 2

^{13}C NMR CHEMICAL SHIFTS FOR THE HEXAFLUOROPHOSPHATE SALTS OF COMPLEXES III, IV AND V AND FOR THE CORRESPONDING FREE KETO LIGANDS

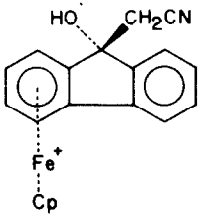
Compound	δ(ppm from TMS)			
	Cp	Complexed aromatic [a]	Uncomplexed aromatic [a]	Carbonyl
Xanthone [b,c]			117.9, 123.8, 126.6, 134.7, 121.7*, 156,0*	177.0
Xanthone-$FeCp^+$ (III) [d]	78.0	77.0, 81.2, 86.1, 88.4 78.1*, 129.4*	117.8, 125.2, 125.8, 136.7, 118.7*, 155.7*	178.7
Thioxanthone [b,c]			126.2, 126.5, 130.0, 132.4, 129.4*, 137.5*	180.1
Thioxanthone-$FeCp^+$ (IV) [d]	78.5	83.7, 83.9, 86.8, 88.0, 83.1*, 107.5*	125.9, 127.3, 129.0, 133.9, 126.5*, 134.8*	181.1
Thioxanthen-9-one-10,10--dioxide [b,e]			123.6, 129.3, 133.3, 134.7, 130.8*, 141.1 *	178.4
Thioxanthen-9-one-10,10--dioxide-$FeCp^+$ (V) [f]	80.4	83.0, 84.8, 84.3, 90.8, 86.7*, 103.9*	123.1, 128.7, 134.1, 135.7, 127.8*, 138.2*	178.0

[a] Asterisks denote quaternary carbons. [b] The spectrum was recorded in $CDCl_3$. [c] From Ref. 3. [d] The spectrum was recorded in CD_3NO_2. [e] From the present work. [f] The spectrum was recorded in DMSO-d_6.

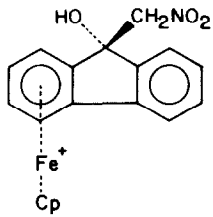
cohol. For example, reaction of the η^6-fluorenone-η^5-cyclopentadienyliron cation (VI) with $NaBH_4$ or $NaBD_4$ gave the complexed 9*H*-fluoren-*endo*-9-ol (VIIa) or 9*D*-fluoren-*endo*-9-ol (VIIb), respectively. In the present work, other reactions with keto complexes were explored so as to provide methods of synthesis of cyclopentadienyliron complexed systems that have not been prepared previously.

Two typical keto complexes, one a complexed ketoarene and the other a complexed heterocyclic ketone, namely, the η^6-fluorenone-η^5-cyclopentadienyliron cation (VI) and the η^6-xanthone-η^5-cyclopentadienyliron cation (III), were chosen as reactants in reactions with various reagents. Analogous to the formation of VIIa or VIIb from the reaction of VI with $NaBH_4$ or $NaBD_4$, treatment of the xanthone complex III with $NaBH_4$ or $NaBD_4$ gave the complexed 9*H*-xanthen-*endo*-9-ol (VIIIa) or the complexed 9*D*-xanthen-*endo*-9-ol (VIIIb), respectively. Similarly, reaction of the fluorenone complex VI or the xanthone complex III, respectively, with CH_3Li in CH_2Cl_2 at low temperature resulted in the *exo*-addition of the methide ion to give the complexed *endo*-alcohol VIIc or VIIIc.

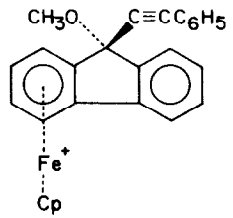
The anion of acetonitrile or nitromethane, generated from the treatment of CH_3CN or CH_3NO_2 with t-BuOK in tetrahydrofuran (THF) at low temperature, was found to react with VI to give the complexed *endo*-alcohol IX or X, respectively. As in the *exo*-addition of the hydride or methide ion, IX and X were derived from



IX



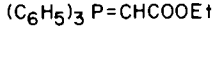
X



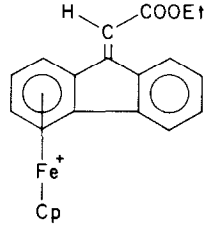
XI

the *exo*-addition of the anions of acetonitrile and nitromethane to the carbonyl group of VI. In a similar way, the phenylacetylide anion, again generated in THF at low temperature from treatment of phenylacetylene with t-BuOK, also reacted with VI to give a complexed *endo*-alcohol, but in this case, to facilitate its isolation, the product was methylated by reaction with $(CH_3)_2SO_4$ to give complex XI. Besides these anionic additions to the carbonyl function, a reaction of VI with an ylid was also studied. The phosphonium ylid XII was prepared from the reaction of ethyl bromoacetate with triphenylphosphine followed by treatment with NaOH. The reaction of XII with VI was found to proceed readily in CH_2Cl_2 at room temperature. The product was a mixture of the *E*- and *Z*-isomers XIIIa and XIIIb.

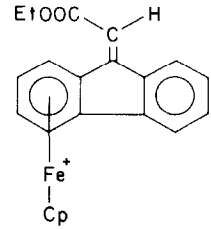
Given in Table 3 are the ^1H NMR chemical shifts and the IR hydroxyl



XII



XIII a



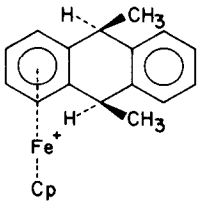
XIII b

absorptions for products VIIIa, VIIIb and VIIIc, obtained from reactions of the xanthone complex III with $NaBH_4$, $NaBD_4$, and CH_3Li, respectively. Similar data for products VIIc, IX, X, XI and XIIIa, XIIIb from reactions with the fluorenone complex VI are summarized in Table 4. These spectral data are consistent with the structures assigned to the various products from the reactions with III or VI. The ^{13}C NMR spectra of all of these products have also been obtained and the ^{13}C data are also consistent with the assigned structures. The ^1H NMR spectrum of VIIIa (Table 3), for example, showed two regions of aromatic absorptions at 6.1–6.5 ppm (complexed aromatic) and 7.1–7.8 ppm (uncomplexed aromatic) and two sets of doublets due to C*H*OH and OH centering at 5.8 and 5.3 ppm, respectively. On the other hand, the ^1H NMR spectrum of VIIIb (Table 3) showed a singlet due to the OH absorption at 5.3 ppm without splitting because of D-substitution. As discussed in the previous work [1], the sharp IR peak at 3578 or 3574 cm^{-1} could be attributed to O–H stretching of the hydroxyl group on the same side as the Fe atom [5–7], thus giving support to the *endo*-configuration for the alcohols.

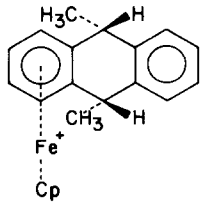
For the products derived from reactions with CH_3Li, VIIc and VIIIc, the *endo*-configuration for the alcoholic hydroxyl was again indicated by the IR O–H stretching absorption at 3574 cm^{-1}. Additional support for the assigned *endo*-configuration was also provided by a comparison of the CH_3 absorptions in the ^1H and ^{13}C NMR spectra of VIIc and VIIIc with those of the η^6-*cis*-(*endo*-9,10-dihydro)-9,10-dimethylanthracene-η^5-cyclopentadienyliron cation (XIV) and the corresponding *exo*-isomer XV [4]. The ^1H and ^{13}C absorptions for the *exo*-CH_3 group of XIV appear at 1.6 and 27.2 ppm, respectively, while the corresponding ^1H and ^{13}C absorptions for the *endo*-CH_3 group of XV appear at 2.0 and 11.9 ppm [4]. From the entries for VIIc and VIIIc in Tables 3 and 4, it is seen that the ^1H NMR absorptions for the CH_3 group in VIIc and VIIIc, respectively, appear at 1.6 and 1.7 ppm, quite similar to the 1.6 ppm absorption of the *exo*-CH_3 in XIV, and different from the 2.0 ppm absorption of the *endo*-CH_3 in XV. Moreover, the ^{13}C NMR absorptions for the CH_3 group in VIIc and VIIIc appear at 28.9 and 33.5 ppm, respectively. These ^{13}C chemical shifts again are similar to that of the *exo*-CH_3 of XIV at 27.2 ppm and different from that of the *endo*-CH_3 of XV at 11.9 ppm. These comparisons thus gave support to the *exo*-configuration for the CH_3 and the *endo*-configuration for the hydroxyl group in VIIc and VIIIc *.

The assignment of the various ^1H NMR chemical shifts for products IX, X, XI

(Continued on p. 165)



XIV



XV

* A referee pointed out that the assignment of the *endo*-structure for the alcoholic hydroxyl groups was based on the purified products and suggested that some *exo*-alcohols could be present in the crude products. While this is a possibility, it is not likely since one would expect the formation of the *endo*-alcohol from a stereospecific *exo*-addition to the carbonyl. In the present work, no attempt was made in detecting any *exo*-alcohol as a minor component in the crude products.

TABLE 3

^{1}H NMR CHEMICAL SHIFTS AND IR HYDROXYL ABSORPTIONS FOR THE PRODUCTS FROM REACTIONS WITH THE η^6-XANTHONE-η^5-CYCLOPENTADIENYLIRON CATION (III)

Reagent	Product [a]	$\delta(CD_3CN)$ (ppm from TMS)				IR
		Cp	Complexed aromatic	Uncomplexed aromatic	Others	ν(OH) (cm^{-1})
$NaBH_4$	9*H*-xanthen-*endo*-9-ol-$FeCp^+$ (VIIIa)	4.8(s, 5H)	6.1–6.3(m, 2H) 6.3–6.5(m, 2H)	7.1–7.5(m, 3H) 7.6–7.8(m, 1H)	5.3(d, 1H, OH) 5.8(d, 1H, C*H*OH)	3578
$NaBD_4$	9*D*-xanthen-*endo*-9-ol-$FeCp^+$ (VIIIb)	4.8(s, 5H)	6.1–6.3(m, 2H) 6.3–6.5(m, 2H)	7.1–7.6(m, 3H) 7.7–7.8(m, 1H)	5.3(s, 1H, OH)	3574
CH_3Li	9-Methylxanthen-*endo*-9-ol-$FeCp^+$ (VIIIc)	4.7(s, 5H)	6.1–6.3(m, 2H) 6.4–6.5(m, 2H)	7.2–7.7(m, 3H) 7.8–7.9(m, 1H)	1.7(s, 3H, CH_3) 4.9(s, 1H, OH)	3574

[a] The products were obtained as their hexafluorophosphate salts.

TABLE 4

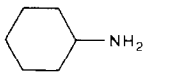
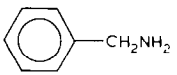
^{1}H NMR CHEMICAL SHIFTS AND IR HYDROXYL ABSORPTIONS FOR THE PRODUCTS FROM REACTIONS WITH THE η^6-FLUORENONE-η^5-CYCLOPENTADIENYLIRON CATION (VI)

Reagent	Product [a]	$\delta(CD_3CN)$ (ppm from TMS)				IR
		Cp	Complexed aromatic	Uncomplexed aromatic	Others	ν(OH) (cm^{-1})
CH_3Li	9-Methylfluoren-*endo*-9-ol-$FeCp^+$ (VIIc)	4.8(s,5H)	6.2–6.4(m,2H) 6.6–6.8(m,1H) 6.8–7.4(m,1H)	7.1–7.8(m,3H) 7.8–8.1(m,1H)	1.6(s,3H,CH_3) 4.7(s,1H,OH)	3574
$NCCH_2^-$	9-Cyanomethylfluoren-*endo*-9-ol-$FeCp^+$ (IX)	4.8(s,5H)	6.2–6.4(m,2H) 6.6–6.7(m,1H) 6.8–6.9(m,1H)	7.5–7.7(m,3H) 7.7–8.0(m,1H)	3.3 [b] (broad s, 2H,CH_2) 5.3(s,1H,OH)	3572
$O_2NCH_2^-$	9-Nitromethylfluoren-*endo*-9-ol-$FeCp^+$ (X)	4.8(s,5H)	6.2–6.4(m,2H) 6.5–6.7(m,1H) 6.8–7.0(m,1H)	7.5–7.8(m,3H) 7.8–8.0(m,1H)	3.3 [b] (broad s, 2H,CH_2) 5.3(s,1H,OH)	3572
$C_6H_5C{\equiv}C^-$	9-*endo*-Methoxy-9-(2-phenylethynyl)-fluorene-$FeCp^+$ (XI)	4.9(s,5H)	6.3–6.4(m,2H) 6.5–7.0(m,2H)	7.4(s,5H) 7.5–8.0(m,4H)	4.0(s,3H,CH_3O)	
ylid XII	6-Carbethoxydibenzo-fulvene-$FeCp^+$ (XIIIa,XIIIb) [c]	4.7(s,5H)	6.6–6.8(m,2H) 7.3–7.4(m,1H) 7.5–7.8(m,1H)	8.0–8.2(m,3H) 8.8–9.0(m,1H)	1.4(2t,3H,CH_3) 4.4(2q,2H,CH_2) 7.3,7.4(2s,1H,=CH)	

[a] The products were obtained as their hexafluorophosphate salts. [b] The broad singlet may be due to the magnetic nonequivalence of the two methylene protons. [c] A mixture of *E*- and *Z*-isomers.

TABLE 5

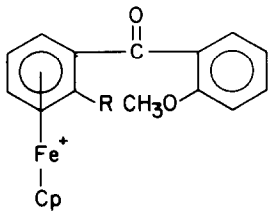
^{1}H NMR CHEMICAL SHIFTS AND IR CARBONYL ABSORPTIONS FOR THE RING OPENING PRODUCTS FROM REACTIONS OF THE XANTHONE COMPLEX III WITH VARIOUS NUCLEOPHILES

Reagent	Product [a]	δ(CD_3CN) (ppm from TMS)				IR
		Cp	Complexed aromatic	Uncomplexed aromatic	Others	ν(CO) (cm^{-1})
$NCCH_2^-$	*o*-Cyanomethyl-*o'*-methoxy-benzophenone-$FeCp^+$ (XVI)	5.3(s,5H)	6.3–6.6(m,4H)	7.0–7.3(m,2H) 7.5–8.0(m,2H)	3.5(s,2H,CH_2) 4.0(s,3H,OCH_3)	1655
$O_2NCH_2^-$	*o'*-Methoxy-*o*-nitromethyl-benzophenone-$FeCp^+$ (XVII)	5.1(s,5H)	6.1–6.3(m,4H)	6.9–7.3(m,2H) 7.5–7.9(m,2H)	3.4(s,2H,CH_2) 3.8(s,3H,OCH_3)	1655
CH_3NH_2	*o'*-Hydroxy-*o*-methylamino-benzophenone-$FeCp^+$ (XVIII)	5.0(s,5H)	5.7–6.3(m,4H)	6.8–7.1(m,2H) 7.3–7.8(m,2H)	2.8(d,3H,NCH_3) 5.1–5.5(broad s, 1H,NH) 11.3(s,1H,ArOH)	1625
	*o*-Cyclohexylamino-*o'*-hydroxybenzophenone-$FeCp^+$ (XIX)	5.0(s,5H)	5.9–6.3(m,4H)	6.9–7.2(m,2H) 7.5–7.8(m,2H)	1.4–2.5(m,1H,CH) 3.1–3.5(m,10H,CH_2's) 11.4(s,1H,ArOH) [b]	1625
	*o*-Benzylamino-*o'*-hydroxy-benzophenone-$FeCp^+$ (XX)	4.7(s,5H)	5.6–6.2(m,4H)	6.8–7.2(m,2H) 7.4–7.8(m,7H)	4.4(d,2H,CH_2) 11.3(s,1H,ArOH) [b]	1632
	*o'*-Hydroxy-*o*-*N*-pyrrolidinyl-benzophenone-$FeCp^+$ (XXI)	5.1(s,5H)	5.8–6.4(m,4H)	6.8–7.1(m,2H) 7.3–7.8(m,2H)	1.8–2.1(m,4H,NCH_2CH_2) 3.1–3.5(m,4H,NCH_2CH_2) 11.7(s,1H,ArOH)	1625

[a] The products were obtained as their hexafluorophosphate salts. [b] The NH absorption was not observed presumably because it was masked under the aromatic absorptions.

and XIIIa, XIIIb given in Table 4, as stated earlier, are consistent with the structures of these products. In the case of XIIIa, XIIIb the presence of two sets of triplets and quartets for the ethyl group indicated the formation of a mixture of the *E*- and *Z*-isomers. Moreover, the vinylic protons of these two isomers appeared as two singlets at 7.3 and 7.4 ppm, although these peaks also overlapped with the complexed aromatic absorptions of XIIIa, XIIIb.

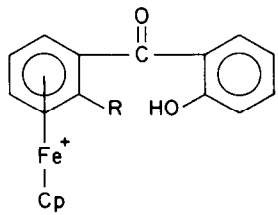
Recently, we have shown that cyclopentadienyliron complexed heterocyclic systems with oxygen as the heteroatom could readily undergo a ring opening reaction when treated with a nucleophilic reagent [8]. For example, upon treatment of the η^6-xanthene-η^5-cyclopentadienyliron cation with pyrrolidine, the CpFe complex of *o*-*N*-pyrrolidinyl-*o'*-hydroxydiphenylmethane was obtained [8]. When the xanthone complex III was treated with the anion of acetonitrile or nitromethane, instead of the anionic addition to the carbonyl as was observed with VI, ring opening reactions took place. To facilitate their isolation, the ring opening products were methylated by treatment with $(CH_3)_2SO_4$, and from the reaction of III with the anions of acetonitrile and nitromethane, respectively, the complexed *o*,*o'*-disubstituted benzophenones XVI and XVII were obtained.



XVI R = CH_2CN

XVII R = CH_2NO_2

Since the previous study on ring opening reactions utilized an amine, pyrrolidine, as the nucleophilic reagent [8], in the present work, the xanthone complex III was treated with 4 different amines, namely, methylamine, cyclohexylamine, benzylamine and pyrrolidine. Ring opening reactions took place in all cases giving the products XVIII, XIX, XX, and XXI, respectively. The structures of ring opening products XVI–XXI are supported by their NMR and IR spectra. Given in Table 5 are the ^1H NMR chemical shifts and the IR carbonyl absorptions and in Table 6 are the ^{13}C NMR data, and these spectral data are consistent with the structures of XVI–XXI.



XVIII R = CH_3NH **XX** R = $C_6H_5CH_2NH$

XIX R =  **XXI** R = 

TABLE 6

^{13}C NMR CHEMICAL SHIFTS FOR RING OPENING PRODUCTS XVI–XXI

Product	$\delta(CD_3NO_2)$ (ppm from TMS)				
	Cp	Complexed aromatic [a]	Uncomplexed aromatic [a]	Others	Carbonyl
XVI	76.7	69.0, 81.4, 85.4, 85.7 97.2*, 130.7*	111.6, 120.0, 129.5, 135.3, 124.9*, 159.0*	54.0 (CH_2) 55.9 (CH_3O) 114.0 (CN)	189.8
XVII	76.7	69.0, 81.4, 85.4, 85.7, 97.2*, 130.7*	111.6, 120.1, 129.5, 135.3, 124.9*, 159.0*	54.0 (CH_2) 56.0 (CH_3O)	189.9
XVIII	76.3	65.0, 78.4, 84.7, 86.2, 82.3*, 124.4*	117.4, 118.7 132.0, 137.6, 119.7*, 161.8*	28.4 (CH_3)	198.4
XIX	76.6	65.0, 78.1, 84.9, 86.2, 80.2*, 123.4*	117.3, 118.8, 131.9, 137.4, 118.6*, 161.6*	23.3, 24.1 30 9, 31.3 (CH_2), 51.1 (CH)	198.8
XX	76.4	65.4, 78.4, 84.8, 86.0 82.3*, 123.3*	117.4, 127.0, 128.1 132.0, 137.7, 118.9*, 136.1*, 161 9*	45.8 (CH_2)	198.4
XXI	75.6	64.9, 77.8, 85.0, 85.6, 83.8*, 124.4*	117.4, 118.9, 132.7, 137.3 119.7*, 161.4*	24.2 NCH_2CH_2 49 8 NCH_2CH_2	198.8

[a] Asterisks denote quaternary carbons.

Experimental

η^6-Xanthone-η^5-cyclopentadienyliron hexafluorophosphate (III-PF_6)

Xanthene (9.11 g, 50 mmol), ferrocene (FcH) (9.3 g, 50 mmol), $AlCl_3$ (27.0 g, 200 mmol) and Al powder (1.4 g, 50 mmol) were heated under reflux in decalin (60 ml) at 140 ± 2°C for 4 h under a N_2 atmosphere. After cooling to 50°C, the reaction mixture was poured into ice-cold water, stirred for 10 min and then filtered. The aqueous layer was separated, washed with ether (3 × 50 ml) and poured into a $KMnO_4$ solution (8.0 g, 50 mmol, in 100 ml of H_2O). The reaction mixture was heated at about 45°C for 5 h. The MnO_2 that was formed was removed by filtration through celite. Upon addition of a concentrated solution of NH_4PF_6, the hexafluorophosphate salt of III precipitated. After filtration and crystallization in nitromethane/ether, 8.8 g (38%) of product was obtained. Its ^1H and ^{13}C NMR data are given in Tables 1 and 2. (Found: C, 46.60, H, 2.90. $C_{18}H_{13}O_2FePF_6$ calcd.: C, 46.78, H, 2.83%.)

η^6-Thioxanthone-η^5-cyclopentadienyliron hexafluorophosphate (IV-PF_6)

Thioxanthene (5.94 g, 30 mmol), FcH (5.58 g, 30 mmol) $AlCl_3$ (16.0 g, 120 mmol) and Al powder (1.0 g, 40 mmol) were heated under reflux in decalin (40 ml) at 140 ± 2°C for 5 h under a N_2 atmosphere. The resulting mixture was cooled to about 50°C, poured into 300 ml of ice-water, stirred for 10 min and then filtered. The aqueous layer was separated, washed with ether (3 × 40 ml) and then poured into a solution of $KMnO_4$ (4.0 g, 25 mmol, in 100 ml of water). The reaction mixture was

heated at 45°C for 3 h and worked up as described in the preparation of III-PF_6. The crude product was dissolved in nitromethane, dried over $MgSO_4$, concentrated and then reprecipitated by the addition of ether. A 7/3 mixture (according to the Cp ^1H NMR absorption) of the η^6-thioxanthone-η^5-cyclopentadienyliron hexafluorophosphate (IV-PF_6) and the corresponding sulfone complex V-PF_6 was obtained. IV-PF_6 was soluble in acetone and it was recovered from the mixture by washing the mixed products with acetone. Recrystallization from acetone/ether gave IV-PF_6 as an orange solid (3.0 g, 21%). Its ^1H and ^{13}C NMR data are recorded in Tables 1 and 2. (Found: C, 44.97, H, 2.64. $C_{18}H_{13}OSFePF_6$ calcd.: C, 45.21; H, 2.74%.)

η^6-Thioxanthen-9-one-10,10-dioxide-η^5-cyclopentadienyliron hexafluorophosphate (V-PF_6)

The ligand exchange reaction between thioxanthene and FcH was carried out as described in the preceding section and the resulting ligand exchange product was treated with a solution of 6.0 g (36 mmol) of $KMnO_4$ in 100 ml of water. After the usual work-up, 4.2 g of a 1/4 mixture of IV-PF_6 and V-PF_6 was obtained. This mixture of products was washed with about 200 ml of acetone. After filtration and concentration of the acetone solution, addition of ether gave a precipitate of 0.62 g (5%) of IV-PF_6. The remaining solid after the removal of the IV-PF_6 was air dried to give 3.4 g (23%) of V-PF_6, which was recrystallized from CH_3NO_2/ether. Again the ^1H and ^{13}C data are summarized in Tables 1 and 2. (Found: C, 42.15, H, 2.64. $C_{18}H_{13}O_3SFePF_6$ calcd.: C, 42.37, H, 2.57%.)

Pyrolytic sublimation

A sample of the hexafluorophosphate salt of η^6-xanthone-η^5-cyclopentadienyliron cation (III-PF_6) (462 mg, 1.0 mmol) was placed in a sublimator with a water cooled cold-finger and then heated to 240°C at 0.5 Torr for 2 h. The xanthone that was formed on the cold finger was removed with ether and purified by recrystallization from ether/hexane to give 186 mg (95%) of xanthone as a white fluffy powder, m.p. 173–174°C (lit. [9a] m.p. 174°C).

Similarly, the pyrolytic sublimation of IV-PF_6 and V-PF_6, respectively, given a 90% yield of thioxanthone, m.p. 208–209°C (lit. [9b] m.p. 209°C), and an 82% yield of thioxanthen-9-one-10,10-dioxide, m.p. 185–186°C (lit. [9b] m.p. 186–187°C).

η^6-9H-Xanthen-endo-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (VIIIa-PF_6)

Upon reduction of the hexafluorophosphate salt of the xanthone complex III with $NaBH_4$ in CH_2Cl_2/H_2O in the same way as decribed previously for the $NaBH_4$ reduction of the fluorenone complex VI [1], a 65% yield of VIIIa-PF_6 was obtained. (Found: C, 46.82, H, 3.38. $C_{19}H_{17}O_2FePF_6$ calcd.: C, 46.58, H, 3.26%.)

A similar reduction using $NaBD_4$ instead of $NaBH_4$ gave a 70% yield of η^6-9*D*-xanthen-*endo*-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (VIIIb-PF_6). The ^1H NMR data for these products are given in Table 3.

η^6-9-Methylfluoren-endo-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (VIIc-PF_6)

A suspension of η^6-fluorenone-η^5-cyclopentadienyliron hexafluorophosphate (VI-PF_6) (0.89 g, 2.0 mmol) in 30 ml of CH_2Cl_2 under N_2 was cooled to about −50°C by means of a 1-hexanol-liquid N_2 slush. To the cold, stirred suspension was added

by a syringe 1.9 ml of 1.2 *M* (2.2 mmol) methyllithium in ether (Aldrich). The reaction mixture was stirred for 45 min and then allowed to warm to −30°C. The resulting brown solution was treated with 10% HCl and with a concentrated solution of NH_4PF_6. The yellow methylene chloride layer was separated, dried over $MgSO_4$ and then evaporated to dryness. Recrystallization from acetone/ether gave 0.54 g (60%) of VIIc-PF_6 as a fine brown powder. The ^1H NMR data for this and other products from reactions with the fluorenone complex VI are given in Table 4. (Found: C, 49.58, H, 3.98. $C_{19}H_{17}OFePF_6$ calcd.: C, 49.37, H, 3.71%).

η^6-9-Methylxanthen-endo-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (VIIIc-PF_6)

Following the same procedure described above for the preparation of VIIc-PF_6, from the reaction of the xanthone complex III with CH_3Li, a 70% yield of VIIIc-PF_6 was obtained as a yellow powder. Its ^1H NMR data are recorded in Table 3. (Found: C, 47.61, H, 3.52. $C_{19}H_{17}O_2FePF_6$ calcd.: C, 47.72, H, 3.58%).

η^6-9-Cyanomethylfluoren-endo-9-ol-η^5-cyclopentadienyliron hexafluorophophate (IX-PF_6)

To a stirred solution of 90 mg (2.2 mmol) of CH_3CN in 30 ml THF, at −15°C under N_2, was added 336 mg (3.0 mmol) of t-BuOK. After stirring for 15 min at −15°C, the solid hexafluorophosphate salt of the fluorenone complex VI (892 mg, 2.0 mmol) was added. The brown solution was stirred for an additional hour and then poured into 10 ml of 10% HCl. The resulting material was treated with a concentrated solution of NH_4PF_6 and then extracted with CH_2Cl_2. The extract as dried over $MgSO_4$ and then evaporated to dryness. After recrystallization from acetone/ether, 526 mg (54%) of IX-PF_6 was obtained. (Found: C, 49.11, H, 3.25. $C_{20}H_{16}ONFePF_6$ calcd.: C, 49.31, H, 3.31%.)

η^6-9-Nitromethylfluoren-endo-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (X-PF_6)

The anion of nitromethane was prepared from 134 mg (2.2 mmol) of CH_3NO_2 and 336 mg (3.0 mmol) of t-BuOK. After treatment with 892 mg (2.0 mmol) of the hexafluorophosphate salt of the fluorenone complex VI and worked up as described above for the preparation of IX-PF_6, 507 mg (50%) of X-PF_6 was obtained. (Found: C, 45.97, H, 3.16. $C_{19}H_{16}NO_3FePF_6$ calcd.: C, 45.99, H, 3.18%.)

η^6-9-endo-Methoxy-9-(2-phenylethynyl)fluorene-η^5-cyclopentadienyliron hexafluorophosphate (XI-PF_6)

A suspension of potassium phenylacetylide was prepared from stirring for 30 min a mixture of 225 mg (2.2 mmol) of phenylacetylene and 336 mg (3.0 mmol) of t-BuOK in 30 ml of THF at −20°C under N_2. Solid VI-PF_6 (892 mg, 2.0 mmol) was then added. The brown solution was stirred at −20°C for an additional 50 min and then 2.0 ml (10 mmol) of $(CH_3)_2SO_4$ was introduced. Stirred was continued for 1 h before a concentrated solution of NH_4PF_6 was added. The resulting material was extracted with CH_2Cl_2 and the extract dried over $MgSO_4$, concentrated and purified by passage through an alumina column with elution by CH_2Cl_2. The eluate was evaporated to dryness, giving the product, XI-PF_6 (674 mg, 60%), which was recrystallized from acetone/ether as yellow crystals. (Found: C, 58.03, H, 3.91. $C_{27}H_{21}OFePF_6$ calcd.: C, 57.67, H, 3.77%.)

Carbethoxymethylenetriphenylphosphorane (XII)

Carbethoxymethylenetriphenylphosphonium bromide, $(C_6H_5)_3P^+CH_2CO_2C_2H_5$ Br^- (429 mg, 10 mmol), prepared according to a procedure described by Wittig and Haag [10], was dispersed in 100 ml of benzene and then 100 ml of a 15% solution of sodium hydroxide was introduced. The mixture was then stirred vigorously for 45 min. The benzene layer was separated, dried over $MgSO_4$, followed by evaporation of the solvent to give the crude product which was recrystallized from CH_2Cl_2/ether, giving $(C_6H_5)_3P{=}CHCO_2C_2H_5$ (XII) as a fine white powder, m.p. 116°C (lit. [11] m.p. 116–117°C).

E- and Z-η^6-Carbethoxydibenzofulvene-η^5-cyclopentadienyliron hexafluorophosphate (XIIIa, XIIIb)

A suspension of 892 mg (2.0 mmol) of the hexafluorophosphate salt of the fluorenone complex VI and 735 mg (2.1 mmol) of ylid XII in 30 ml of CH_2Cl_2 was stirred at room temperature overnight. The resulting brown solution was concentrated and purified by passage through an alumina column. The triphenylphosphine oxide was first washed off with methylene chloride. Subsequent elution by acetone gave a yellow solution. After concentration and addition of ether, 714 mg (69%) of an *E* and *Z* mixture of the hexafluorophosphate salts of XIIIa and XIIIb was obtained. (Found: C, 51.35, H, 3.68. $C_{22}H_{19}O_2FePF_6$ calcd.: C, 51.19, H, 3.71%.)

Ring opening reactions

The hexafluorophosphate salt of the xanthone complex III, when treated with the anion of acetonitrile or nitromethane, or when treated with methylamine, cyclohexylamine, benzylamine or pyrrolidine, gave the cyclopentadienyliron complexed *o,o'*-disubstituted benzophenones XVI–XXI as given in Table 5. The ^1H and ^{13}C NMR data for these ring opening products are summarized in Tables 5 and 6. Two typical experimental procedures are described below.

η^6-o'-Methoxy-o-nitromethylbenzophenone-η^5-cyclopentadienyliron hexafluorophosphate (XVII-PF_6)

To a stirred solution of CH_3NO_2 (134 mg, 2.2 mmol) in 30 ml of THF, under N_2 at −15°C, t-BuOK (336 mg, 3.0 mmol) was added. After stirring for 15 min, solid III-PF_6 (924 mg, 2.0 mmol) was introduced. The resulting red solution was stirred at −15°C for 1 h and then treated with $(CH_3)_2SO_4$ (2.0 ml, 10 mmol). The mixture was stirred for an additional 2 h at temperatures below −10°C and then a concentrated solution of NH_4PF_6 was added. The mixture was extracted with CH_2Cl_2 and the extract was dried over $MgSO_4$. After removal of the solvent, recrystallization from acetone/ether gave 752 mg (70%) of XVII-PF_6. (Found: C, 44.43, H, 3.51. $C_{20}H_{18}NO_4FePF_6$ calcd.: C, 44.71, H, 3.88%.)

η^6-o'-Hydroxy-o-N-pyrrolidinylbenzophenone-η^5-cyclopentadienyliron hexafluorophosphate (XXI-PF_6)

A suspension of 924 mg (2.0 mmol) of III-PF_6 in 30 ml of CH_2Cl_2 was treated under N_2 at room temperature with 0.2 ml (2.5 mmol) of pyrrolidine. A brown solution was formed after a few min. After stirring for 8 h, the reaction mixture was treated with a concentrated solution of NH_4PF_6 and then with 10 ml of 10% HCl.

The methylene chloride layer was separated, dried over $MgSO_4$ and then evaporated to dryness. After recrystallization from acetone/ether, 901 mg (84%) of XXI-PF_6 was obtained as a brown powder. (Found: C, 49.51, H, 4.21. $C_{22}H_{22}NO_2FePF_6$ calcd.: C, 49.55, H, 4.16%.)

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